TABLE I
PHYSICAL CONSTANTS OF SUBSTITUTED TRIAZINES

Position 2	Position 4	Position 6	Bp, °C (mm)	$n^{25}D$	Registry no.
i-C_3F_7	F	F	99–100 (630)	1.3131	10271-35-9
i-C_3F_7	i-C_3F_7	F	125–126 (630)	1.3373	10271-36-0
i-C_3F_7	i-C_3F_7	i-C_3F_7	137–138[a] (630)	...	10271-37-1
$(CF_3)_2N$	F	F	108–109 (630)	1.3477	10271-38-2
$(CF_3)_2N$	$(CF_3)_2N$	F	73–75 (40)	1.3485	10271-39-3
$(CF_3)_2N$	$(CF_3)_2N$	$(CF_3)_2N$	90[b] (40)	...	10271-40-6
$CF(CF_3)CF_2CN$	i-C_3F_7	i-C_3F_7	79–80 (20)	1.3266	10271-41-7

[a] Mp 30–31. [b] Mp 47–48.

initial 132.5 g being recovered. The material was fractionated through a 1-ft column of metal helices to give the monoalkylated product in 39% conversion, the dialkylated product in 51% conversion, and the trialkylated product in 5% conversion.

Although the structures of all three compounds were established unequivocally by nmr and infrared spectra, elemental analyses on the mono- and dialkylated products were unsatisfactory except for nitrogen values, possibly because of hydrolysis of the very moisture-sensitive ring fluorine atoms since the trialkylated product gave satisfactory results.

Anal. Calcd for $C_{12}F_{21}N_3$: C, 24.6; F, 68.2; N, 7.2. Found: C, 24.6; F, 68.0; N, 7.3.

Cyanoperfluoroalkylation of 2,4-Bis(perfluoroisopropyl)-6-fluoro-*s*-triazine.—A pressure vessel containing 10 g of dried cesium fluoride was loaded by siphoning in under partial vacuum 14 g (0.032 mole) of the above triazine and adding by vacuum transfer 4.5 g (0.028 mole) of perfluoroallyl cyanide. It was then sealed and rocked for 24 hr at 100°. The crude product was decanted, combined with Freon 113 extracts of the residual solid, and fractionated to give 10.4 g (61.5%) of the addition product.

Anal. Calcd for $C_{13}F_{20}N_4$: C, 26.4; N, 9.5. Found: C, 26.7; N, 9.8.

Perfluorodimethylamination of Cyanuric fluoride.—A pressure vessel containing 50 g of dried cesium fluoride was loaded, as described above, with 10 g (0.075 mole) of cyanuric fluoride and 20 g (0.15 mole) of perfluoro-2-azapropene. After agitation at 110° for 26 hr it was evacuated through a cold trap for 6 hr. The residual material was extracted with two 25-ml portions of Freon 113, the solvent was removed, and the liquid residue was combined with that obtained during the evacuation. Fractionation through a vacuum-jacketed Vigreux column gave, in addition to intercuts, 3.8 g (19% conversion) of the monosubstituted compound, 8.5 g (29% conversion) of the disubstituted compound, and 4.3 g (16% conversion) of the trisubstituted compound, all at least 88% pure. Since no extraneous peaks appeared in chromatograms of any of the intercuts, and material balance was good, the apparent conversion figures would be raised appreciably by more efficient separation.

Acknowledgment.—This work was supported by the U.S. Air Force Materials Laboratory and by the National Aeronautics and Space Administration.

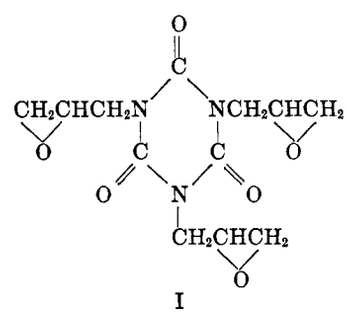
Triglycidyl Isocyanurate Synthesis Using Dispersed Caustic

H. P. PRICE AND G. E. SCHROLL

Polymer Research Laboratory, Celanese Coatings Company, Louisville, Kentucky

Received December 22, 1966

The products from the reaction of cyanuric acid with epichlorohydrin have been dehydrohalogenated by a variety of methods to give epoxy compositions.[1] Recent publications[2] indicate that crystalline triglycidyl isocyanurate, or tris(2,3-epoxypropyl)-*s*-triazine-2,4,6-(1H,3H,5H)-trione, may be obtained as a mixture of two racemic modifications by this general preparative route. The procedure below also permits the isolation of crystalline triglycidyl isocyanurate (I) and illustrates the use of a novel dispersed form of sodium hydroxide for dehydrohalogenation.



I

A stable dispersion of caustic in an aprotic medium may be prepared if a small amount of a fatty acid is employed as a dispersing aid. Particle diameters under 15 μ have been obtained in benzene, mineral spirits, dioxane, and xylene. Such dispersions can be metered into a reactor with a chemical proportioning pump, and permit a more rapid reaction or use of a lower reaction temperature than other solid forms of caustic in the preparation of triglycidyl isocyanurate. Other reactions involving additions of solid caustic can perhaps be similarly facilitated by use of the dispersed form of the reagent.

Experimental Section

Caustic Dispersion.—A mixture of 400 g of 96% flake sodium hydroxide, 4 g of dimerized fatty acid, and 600 g of xylene was ground overnight in a pebble mill[3] with a 60-rpm speed. The dispersion was stored in a glass container after removal of the pebbles. Standardization and metering by volume proved feasible if the stored dispersion was shaken by hand before sampling and xylene was used as a wash liquid to complete a transfer.

Crystalline Triglycidyl Isocyanurate (I).—A mixture of 129 g (1.0 mole) of cyanuric acid, 1388 g (15.0 mole) of epichlorohydrin, and 7 ml of a 60% aqueous solution of benzyltrimethylammonium chloride was heated until a self-sustaining exothermic reaction was established at 113°. When the reaction temperature began to drop after about 10 min, heat was again applied to maintain reflux conditions for 1 hr. The above caustic dispersion (3 equiv, 308 ml) was then added over 1.5 hr to the stirred mixture at ambient temperature between 31 and 51°. Water was then azeotropically distilled from the reactor at overhead temperatures up to 120°, and the cooled residue was filtered to remove salt. The excess epichlorohydrin was subsequently distilled off at pot temperatures up to 122° at 35 mm and replaced by 400 ml of methyl ethyl ketone.

(1) U. S. Patent 2,809,942; U. S. Patent 2,931,781; French Patent 1,394,438; British Patent 996,724.

(2) M. Budnowski, *Kunststoffe*, **55**, 641 (1965); German Patent 1,211,650.

(3) Neck-type ABCO porcelain jar of the Abbe Engineering Co., with size B-2 flint pebbles and 1-qt rated capacity.

A total of 41 ml (0.40 equiv) of caustic dispersion was added over 7 min to the ketone solution at 45°. Stirring was continued for 20 min, and the mixture was then heated to 86° over 0.5 hr to azeotropically remove additional water. The hot mixture was immediately filtered, using additional ketone to wash the filter cake. Removal of volatile components at pot temperatures up to 108° at 35 mm gave 254 g (85% yield) of low-melting epoxy residue with 1.07% chlorine content and a 122 epoxide equiv wt. Three recrystallizations at 5, 25, and 25° from 20% methanolic solutions gave 77 g of crystalline triglycidyl isocyanurate with a mp 100–104°, a 103 epoxide equiv wt (theory, 99), and a 0.3% chlorine content.

Racemic Modifications of Triglycidyl Isocyanurate.[2]—Extraction of 20 g of the above crystalline product with 80 g of hot methanol permitted separation of the two racemic modifications. The more soluble modification was recrystallized from methanol, and the other from Methyl Cellosolve, to obtain analytical samples for characterization.

The more soluble modification melted at 103–104.5° and had a 99.7 epoxide equiv wt. Its infrared spectrum (mineral oil mull) contained a strong absorption band at 5.90 μ, no band in the region of 6.4 μ, and moderate absorption bands at 10.25, 11.80, 12.55, and 13.10 μ. Infrared data indicated that heating for 6 hr at 160° under nitrogen caused slight decomposition.

Anal. Calcd for $C_{12}H_{15}N_3O_6$: C, 48.48; H, 5.09; N, 14.14. Found: C, 48.6, 48.5; H, 4.96, 5.18; N, 13.9, 13.9.

The less soluble modification melted at 156–157.5° and had a 101 epoxide equiv wt. Its infrared spectrum contained a strong absorption band at 5.90 μ, a very minor band (0.03 optical density) at 6.45 μ, and moderate absorption bands at 10.10, 10.75, 11.15, 12.15, 12.70, and 13.25 μ. The infrared spectrum remained unchanged when the modification was held at 165° for 8 hr under nitrogen.

Anal. Found: C, 48.4, 48.4; H, 5.07, 5.01; N, 14.4, 14.7.

Registry No.—I, 2451-62-9.

Studies in the Heterocyclic Series. I. A Novel Diazaphenothiazine System

CHARLES OKOLO OKAFOR

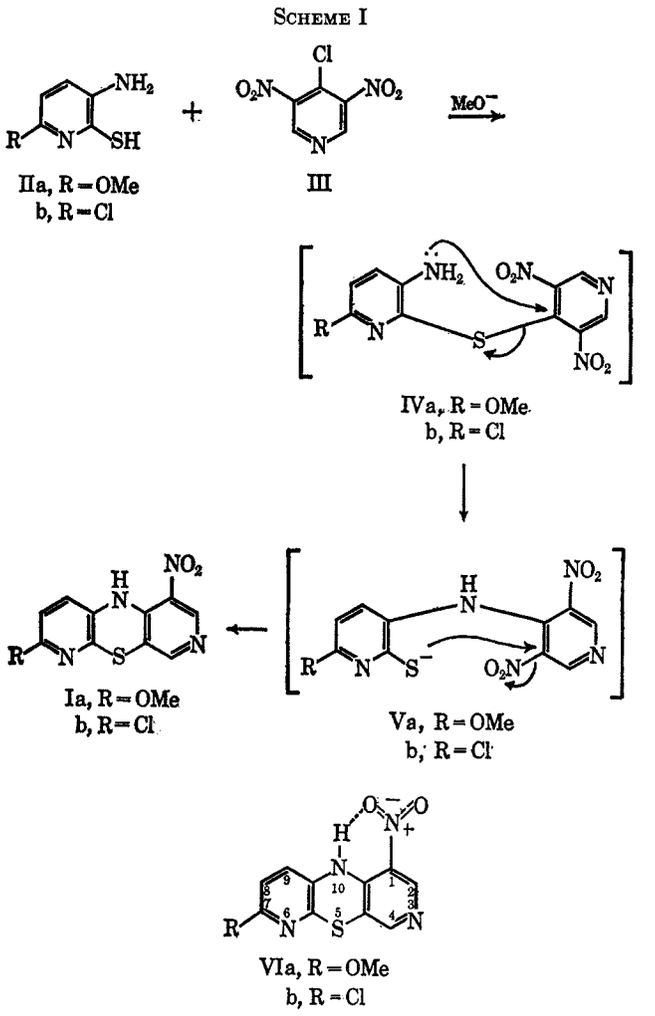
Department of Chemistry, University of Nigeria, Nsukka, Eastern Nigeria

Received December 5, 1966

Continued interest in phenothiazines[1] has led to syntheses of 1-aza-,[2] 2-aza-,[3] 3-aza-,[4] 4-aza-,[5] 1,3-diaza-,[6] and 1,6-diazaphenothiazines.[7] In the present paper is reported the synthesis of 3,6-diazaphenothiazines (Ia, R = OMe; Ib, R = Cl) which form another variation of the phenothiazine system. A convenient route to this type of compound involves the condensation of the appropriate 3-amino-2-mercaptopyridine (IIa, R = OMe; IIb, R = Cl) with 3,5-dinitro-4-chloropyridine (III)[8] in the presence of excess base *via* Smiles rearrangement and cyclization. The aminomercaptopyridines were obtained by converting the appropriate aminopyridines to the corresponding 2-aminothiazolo[5,4-*b*]pyridines followed by base-catalyzed hydrolysis.[5] This method is preferred to the alternative method reported which led to a violent explosion during the conversion of nicotinamide to the chloroaminoderivative.[9] Equimolar quantities of the aminomercaptopyridines (IIa, R = OMe; IIb, R = Cl) and III were condensed in methanolic potassium hydroxide to yield the 4′-(3,5-dinitro)pyridyl-3-amino-2-pyridyl sulfides (IVa, R = OMe; IVb, R = Cl). In excess base, the aminodiaryl sulfides IV underwent Smiles rearrangement to the potassium salts of 4′-(3,5-dinitro)pyridyl-2-mercapto-3-aminopyridines (V). The latter products are rather unstable and their instability was used to advantage when they spontaneously cyclized to the more stable 3,6-diazaphenothiazines (Ia, R = OMe; Ib, R = Cl) (Scheme I).

Because of the proximity of the N-10 proton to the 1-nitro group, it is possible that a six-membered chelate

SCHEME I



(1) (a) S. P. Massie, *Chem. Rev.*, **54**, 791 (1954); (b) A. Burger and J. L. Stanmyer, *J. Org. Chem.*, **21**, 1382 (1956); (c) A. Burger, J. G. Beasley, R. B. Margerison, J. Doull, V. Plzak, and J. F. Noble, *J. Med. Pharm. Chem.*, **1**, 171 (1959).

(2) (a) W. A. Schuler and H. Klebe, German Patent, 964,050, (1957); U. S. Patent 2,974,139 (1961); *Ann.*, **653**, 172 (1962); (b) H. L. Yale and F. Sowinski, *J. Am. Chem. Soc.*, **80**, 1651 (1958); (c) A. v. Schlichtegroll, *Arzeneimittel-Forsch.*, **7**, 237 (1957); **8**, 489 (1958).

(3) (a) P. N. Craig, M. Gordon, J. J. Lafferty, B. Lester, M. Pavloff, and L. Zirkle, *J. Org. Chem.*, **25**, 944 (1960); (b) A. J. Saggiomo, P. N. Craig, and M. Gordon, *ibid.*, **23**, 1906 (1958).

(4) (a) V. A. Petrow and E. L. Rewald, *J. Chem. Soc.*, 591 (1945); (b) F. H. Clarke, G. B. Silverman, C. M. Watnick, and N. Superber, *J. Org. Chem.*, **26**, 1126 (1961).

(5) (a) T. Takahashi and E. Yoshii, *Chem. Pharm. Bull.* (Japan), **2**, 382 (1954); *Chem. Abstr.*, **50**, 13032e (1956); (b) Y. Yamamoto, *J. Pharm. Soc. Japan.*, **71**, 916 (1951).

(6) (a) A. P. Phillips, N. B. Mehta, and J. Z. Strelitz, *J. Org. Chem.*, **28**, 1488 (1963); (b) B. Roth and G. H. Hitchings, *ibid.*, **26**, 2770 (1961); (c) A. Westermann, O. Bub, and L. Suranyi, D. R. Patent, 1,110,651 (1961); *Chem. Abstr.*, **56**, 2461*a* (1962).

(7) (a) T. Takahashi and Y. Maki, *Chem. Pharm. Bull.* (Japan), **6**, 369 (1958); (b) Y. Maki, *J. Pharm. Soc. Japan*, **77**, 485 (1957); (c) O. R. Rodig, R. E. Collier, and R. K. Schlatzer, *J. Med. Chem.*, **9**, 116 (1966).

(8) (a) W. H. Crowe, *J. Chem. Soc.*, **127**, 2028 (1925); (b) S. Kruger and F. G. Mann, *ibid.*, 2755 (1955); (c) see ref 4.

(9) (a) Y. Ahmad and D. H. Hey, *ibid.*, 4516 (1954); (b) O. R. Rodig, R. E. Collier, and R. K. Schlatzer, *J. Org. Chem.*, **29**, 2652 (1964).